

Toward conductive traces: Dip Pen Nanolithography[®] of silver nanoparticle-based inks

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(Received 29 August 2008; accepted 9 September 2008; published online 7 October 2008)

Low cost, direct writing of conductive traces is highly desired for applications in nanoelectronics, photonics, circuit repair, flexible electronics, and nanoparticle-based gas detection. The unique ability of Dip Pen Nanolithography (DPN[®]) to direct write a variety of materials onto suitable surfaces with nanoscale resolution and area-specific patterning is leveraged in this work. We present a direct-write approach toward creating traces with commercially available silver nanoparticle (AgNP)-based inks using DPN. In this work we demonstrate submicron AgNP feature creation together with a discussion on the ink transport mechanism. © 2008 American Institute of Physics. [DOI: 10.1063/1.2995859]

High concentration metallic nanoparticle-based inks—such as silver, gold, and copper—are well developed and have been widely used for printed circuit boards and flexible electronics. This simple two step metallization process—direct-printing and low-temperature curing—is especially suitable for massive, large area, and low-cost electronics fabrication.^{1,2} Two common printing techniques are drop-on-demand (DOD) ink-jet printing with micronozzles² and microcontact printing (μ -CP) with soft stamps.³ However these techniques have drawbacks: in DOD ink-jet printing, ink clogs are formed in the nozzle and the resolution is limited by nozzle outlet diameter which is in the micron range. The resolution of μ -CP, on the other hand, is confined by optical lithography with an extreme lower limit of $\sim 2 \mu\text{m}$, and defects are frequently observed due to issues of both stamp/substrate gap and printing force. Another method of submicron feature generation is the nanofountain pen technique,⁴ but this suffers from inherent problems of pen clogging and ink flow due to nanoparticle agglomeration, especially when printing lines. In order to expand the applications of metallic nanoparticle-based inks to include nanoelectronics,⁵ photonics,⁶ and/or chemical/biosensors,⁷ other printing methods need to be explored that are capable of submicron feature generation and that are highly reproducible, high yield, low cost, and have the ability to direct placement with respect to existing features.

The direct-write method of Dip Pen Nanolithography (DPN[®])⁸ is an ideal candidate for creating submicron metallic traces since the process is highly tailorable, enables selective pattern creation, is not ink or surface specific, requires no special operating conditions, and can flexibly direct feature placement. DPN has been shown to pattern a wide variety of inks on a wide variety of substrates, and thorough reviews of DPN exist in recent literature.^{9,10} In this paper, we demonstrate direct writing of commercially available silver nanoparticle (AgNP)-based inks using an NSCRIPTOR[™] DPN system (NanoInk, Skokie, IL). We compare different AgNP

ink sources (including organic and water based inks), provide results toward conductive trace writing, and discuss the ink transport of AgNP inks with respect to the diffusive ink transport of the alkanethiol inks frequently used to demonstrate DPN.

We created silver traces by moving an inked atomic force microscopy (AFM) tip across the substrate at a specified tip speed. A schematic of the overall AgNP ink DPN process is illustrated in Fig. 1. We used a silicon oxide (SiO_x) substrate, which we plasma cleaned (10 min in pure oxygen) in order to remove organic contamination. For the actual AgNP ink source, we chose a commercially available hydrophilic AgNP ink (PChem Associates, Bensalem, PA). We inked the tips using NanoInk Inkwells[™] in order to control both the amount of ink delivered to the tip, and the extent of the ink wicking onto the surrounding cantilever.¹¹ We pipetted the ink solution into the Inkwell reservoir, whereafter it flowed into the tip-sized microfluidic well. This was coordinated by standard NSCRIPTOR inking routines (i.e., AFM scanner-controlled vertical movements). Since we performed

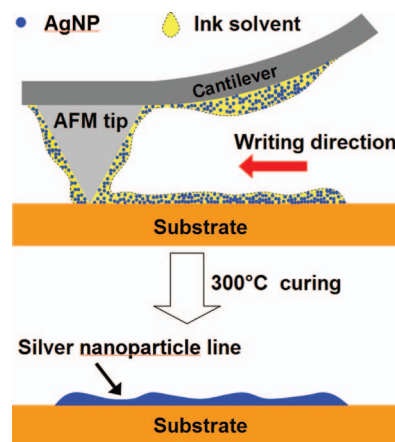


FIG. 1. (Color) Schematic representation of the DPN procedure used to pattern AgNP ink on a SiO_x substrate. This procedure is common to other substrates.

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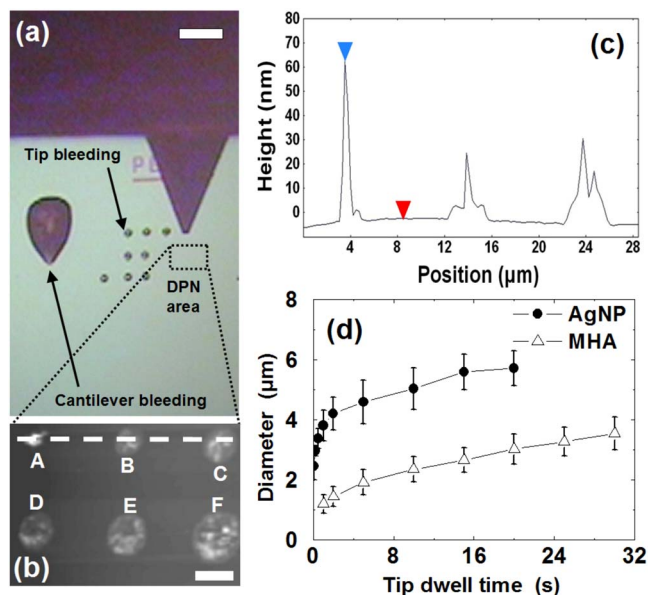


FIG. 2. (Color online) (a) Optical microscopy image of the process of bleeding excess AgNP ink with both the cantilever and tip (scale bar=50 μm). (b) Representative AFM topography image of silver dots generated by increasing tip-substrate contact times [(A)–(F)] (scale bar=4 μm). The identification letter, tip contact time, and measured diameter of the dots are (A) 0.1 s, 1.972 μm ; (B) 0.2 s, 2.828 μm ; (C) 0.5 s, 3.87 μm ; (D) 1 s, 4.466 μm ; (E) 2 s, 4.947 μm ; (F) 5 s, 5.396 μm . The image shows the dots postcuring and the dotted line shows the region where the topography line trace was measured. (c) Cross-sectional topography trace of the dots in (b) showing an average feature height of approximately 30 nm. (d) Average AgNP dot diameter curves plotted as a function of dwell time compared to those of a typical chemisorbed DPN ink (MHA). The error bars represent standard deviations of five AgNP and twelve MHA DPN experiments.

these experiments under ambient conditions, the prospect of ink drying on the tip or in the Inkwell microchannel needed to be considered. To resolve this problem, we added a high boiling point hydrophilic solvent to the as-received PChem AgNP ink to reduce the overall ink drying rate. We chose glycerol, with a boiling point of 182 $^{\circ}\text{C}$ at 20 mm Hg. In our observation, a drop of this modified ink in an Inkwell could remain in a “wet” state over a period of days.

Figure 2(a) shows a standard silicon nitride (SiN) tip (NanoInk, type S-2) after the inking process. Excess AgNP ink is reduced through tip “bleeding” by simply bringing the inked tip into contact with the substrate. After an average of eight sub-10- μm bleeding spots, the tip starts writing uniform submicron sized dots. We subsequently executed patterning on the NSCRIPTOR using patterns designed in InkCAD (NSCRIPTOR design software). DPN is commonly force independent,^{8,10} and we performed this patterning un-

der constant height mode without force feedback; this faster process eliminates the need to align a laser spot on the cantilever. Following 10 min of hot plate curing at 300 $^{\circ}\text{C}$, we scanned the traces in AC mode AFM at a rate of ~ 1 Hz. Figure 2(b) shows the actual dot pattern written inside a 25 μm area after bleeding the tip of the excess ink. Dots correspond to tip contact times ranging from 0.1 to 5 s, and the line topography cross-sectional view of Fig. 2(b) is shown in Fig. 2(c).

In order to investigate the ink-surface interactions relevant to ink transport, we compared the contact angles of the three different ink solutions shown in Table I: the as-received PChem ink (in its water/surfactant-based solution), the PChem ink+glycerol, and an organic solvent-based AgNP ink from NanoMas Technologies Inc. (Vestal, NY). Notably, contact angle measurements using a 1 μl drop on a SiO_x surface showed a contact angle of $\sim 28^{\circ}$ for the PChem+glycerol ink compared to 0° for the NanoMas ink. The NanoMas ink forms a thin film on both the tip (SiN) and substrate (SiO_x) due to its similar hydrophobicity with both surfaces. This leads to ink flow problems from the tip to the substrate, and fast drying on the tip. By contrast, the PChem+glycerol ink stays in a beaded drop on both the tip and substrate; this aids the flow from tip to substrate and yields better DPN reproducibility. Aided by these contact angle measurements, we formulated an ink with a slow tip dry rate and good flow characteristics for the AgNP DPN process.

Compared to the DPN process for conventional 16-mercaptohexadecanoic acid (MHA) ink—which is coated dry on the tip, chemisorbed on gold surfaces, and utilizes a native water meniscus for ink transport^{8,12}—the AgNP ink is deposited from a solvent-retaining tip. Because the AgNP ink is already in the liquid phase, the process does not seem to require a water meniscus for ink transport. Further, the dwell time dependence shown in Fig. 2(b) implies that this AgNP ink is amenable to feature size control. In order to show the difference in transport mechanisms between AgNP DPN and chemisorption-controlled DPN, we compare the AgNP ink to MHA, as shown in Fig. 2(d). When patterned on a gold substrate, the MHA DPN process is directed by chemical sorption of the $-\text{S}-$ bonds. By contrast, the AgNP DPN process is dominated by physical adsorption since there is no specific chemical binding between the AgNP ink and the substrate. We also notice from Fig. 2(d) that the y-axis intercepts extrapolated from the two curves are different; the elevated AgNP y-intercept is due to a higher initial ink loading on the tip, with an intentionally slow-drying solvent. In the case of MHA, the ethanol solvent evaporates quickly, effec-

TABLE I. Comparison of the three different AgNP ink systems used in this work.

	Solvent	Solvent boiling point	Drying issue	Contact angle on SiO_x substrate	Inking on cantilever	Writing on SiO_x substrate
PChem ink	Water, 45%–60%	100 $^{\circ}\text{C}$ at 1 atm	Yes	$22 \pm 5^{\circ}$	Yes	No
PChem ink + glycerol	Water 22%–30% Glycerol, $\sim 50\%$	100 $^{\circ}\text{C}$ at 1 atm 182 $^{\circ}\text{C}$ at 20 mmHg	No	$28 \pm 5^{\circ}$	Yes	Yes
NanoMas ink	Dodecane, 25%–65% Cyclohexane, 0%–50% Terpineol, 0%–20%	215–217 $^{\circ}\text{C}$ at 1 atm 80.7 $^{\circ}\text{C}$ at 1 atm 213–218 $^{\circ}\text{C}$ at 1 atm	No	$\sim 0^{\circ}$	Yes	No

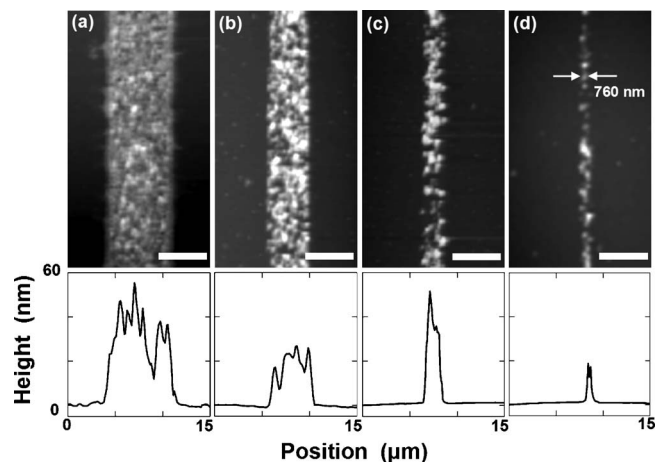


FIG. 3. AFM topography image of AgNP lines generated via a tip speed of $10 \mu\text{m/s}$ in a $25 \mu\text{m}$ area. (a) $\sim 10 \mu\text{m}$ linewidth, (b) $5 \mu\text{m}$ linewidth, (c) $2 \mu\text{m}$ linewidth, and (d) $\sim 760 \text{ nm}$ linewidth. The cross-sectional topography traces of (a)–(d) are shown below, while the scale bars in (a)–(d) are $5 \mu\text{m}$ each. All lines shown were imaged postcuring.

tively leaving a smaller dry tip which patterns a smaller range of features. Like other physisorbed inks,¹³ the AgNP ink curve starts to reach an equilibrium where the ink has minimized its energy with respect to the surface, and further contact time will not increase the feature size. Therefore, it is reasonable to conclude that physisorption and AgNP ink-surface tension factors determine the minimum possible feature size. Physisorbed inks also tend to be more substrate general,¹³ and we demonstrated AgNP patterning on Kapton™ and indium tin oxide substrates, both of which are specifically useful in nanoelectronic applications.

Toward evaluating a conductive trace application, we wrote four $40 \mu\text{m}$ long lines with the AgNP ink on SiO_x (Fig. 3); this line length matches or exceeds typical electrode gaps and serves as a benchmark length for continuous trace writing. The linewidths obtained ranged from $10 \mu\text{m}$ [Fig. 3(a)] down to 760 nm [Fig. 3(d)], where the linewidth is controlled using different tip speeds. Initial Ag line conductivity measurements on a separate $80 \mu\text{m}$ line suggest that the AgNP line is conducting.¹⁴ However the line resistivity is different than that expected for bulk Ag (electrical

resistivity = $16.17 \text{ n}\Omega \text{ m}$).¹⁵ We are gathering additional conductivity data, and future work will explore these results. Annealing after the initial patterning is also expected to affect the continuity of the Ag line pattern with respect to how the AgNP ink coalesces. Future efforts will assess the effect of annealing methods on the formation of continuous AgNP line features for electronic characterization of the patterned silver traces.¹⁶

In conclusion, we have demonstrated a reliable way to pattern Ag lines using DPN, which is useful for a wide variety of applications. This direct-write approach resulted in submicron line features, and we show that the ink deposition mechanism is different from normal chemisorption-directed DPN. Although this method still needs to be optimized for even smaller linewidths and definitive measurement of bulk Ag resistivity, we have nevertheless shown DPN as a unique way to pattern submicron Ag line features.

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¹⁴See EPAPS Document No. E-APPLAB-93-054840 for an optical image and resistance measurement of an $80 \mu\text{m}$ long AgNP trace across two electrodes. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.

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